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(54) Title: RADIATION CURABLE DENDRITIC OLIGOMER OF POLYMER

(57) Abstract: A radiation curable dendritic oligomer or polymer obtainable by addition of at least one secondary amine to at least one acrylic double bond in a dendritic acrylate oligomer or polymer is disclosed. Said radiation curable oligomer or polymer nominally has at least one acrylic double bond and at least one tertiary amine group. In a further aspect, the present invention refers to a process for production of said radiation curable dendritic oligomer or polymer. Said process comprises the step of acrylation of a dendritic polymer nominally having at least two terminal hydroxyl groups and the step of Michael addition of at least one secondary amine to at least one acrylic double bond. In yet a further aspect, a radiation curable composition comprising said dendritic oligomer or polymer is disclosed.

## **RADIATION CURABLE DENDRITIC OLIGOMER OR POLYMER**

The present invention refers to a radiation curable dendritic oligomer or polymer nominally having at least one acrylic double bond and nominally at least one tertiary amine group. In a further aspect, the present invention refers to a process for production of said radiation curable dendritic oligomer or polymer. In yet a further aspect, the present invention refers to a radiation curable composition comprising said radiation curable dendritic oligomer or polymer.

Radiation curable coatings are a class of industrial coatings having in recent years expanded rapidly. The rapid growth of radcure coatings in relation to the total coatings market is a matter certain significant advantages over for instance traditional solventborne coatings. Radiation curable coatings are solvent-free and will not give any major emissions to the atmosphere. Hence, VOC emissions can be drastically reduced if an industrial coater replaces solventborne systems with the solvent-free radcure technology. Furthermore, radiation curable coatings have a very high reactivity and are energy efficient as they do not need to be heated. At the same time investment costs to convert from solventborne technology to radcure technology is low. This means that production costs can be reduced by using radcure coatings instead of solventborne systems. Radiation curable coatings can in other words offer an environmental solution as well as reduce production costs. The most industrially viable class of radiation curable coatings today are acrylate and methacrylate functional polymers, oligomers and monomers.

In spite of the many advantages obtained with radiation curable coatings, as discussed above, there are, however, some disadvantages remaining to be improved. One of the issues discussed in the industry today is the reduce or complete removal of photoinitiators in radiation curable coatings. All radiation curable coatings today, cured by medium pressure ultraviolet (UV) lamps, need photoinitiators forming radicals upon irradiation with UV light and promoting radical polymerisation of the coating. When curing under air atmosphere, air inhibition reduces the reaction speed of the radical polymerisation and comparatively large amounts of photoinitiators are needed to promote sufficient cure speed. Typical amounts of photoinitiators are 4-10 % by weight of a coating formulation.

Photoinitiators are in general rather expensive and in some cases toxic. They give rise to degradation products after cure, which degradation products can give the cured coating an unpleasant odour. Remaining degradation products of photoinitiators can also impart the UV-stability of the cured coating and give rise to yellowing and coating degradation from natural exposition to UV light. Degradation products originating from photoinitiators can

furthermore present a health hazard and can therefore restrict the use of radiation curable coatings in for instance food packaging applications.

It has quite surprisingly through the present invention been found that the problem with photoinitiators discussed above can be overcome or substantially reduced by the use of dendritic acrylates of a particular molecular design. A dendritic acrylate oligomer or polymer partly derivatised with at least one tertiary amine yields, without or with extremely low amounts of photoinitiators, coatings with excellent reactivity and film properties. Said dendritic acrylates can be cured with low intensity UV lamps (80W/cm) under air atmosphere. Obtained coatings have very good film hardness, scratch resistance and chemical resistance.

Dendritic polymers are known to give excellent properties to various resin systems including coatings as disclosed in for instance the Swedish patents nos. 468 771, 502 634, 503 342, 503 622, 504 879 and 509 240 as well as in the International Patent Applications WO 97/23538 and WO 97/23539 and WO 96/07688, all teaching various types of dendritic polyesters with and without chain termination as well as the use and properties of said polyesters in applications such as binders, thermosets, thermoplastics and lubricants. Dendritic polymers are, furthermore, disclosed in WO 95/20619 teaching dendritic macromolecules prepared from halogen cyanide units and EP 0 115 771 teaching dendritic polyamidoamines and dendritic polyethers. The state of the art is excellently compiled in for instance "*Dendritic Molecules - Concepts · Syntheses · Perspective*" by G.R. Newkome, C.N. Moorefield and F. Vögtle - VCH Verlagsgesellschaft mbH, 1996.

The densely branched polymer structure of dendritic molecules yields polymers with exceptionally low viscosity, yet high molecular weights. The branched structure also results in a very high functionality at any given molecular weight. The high functionality, in combination with excellent rheological properties, makes it possible to tailor oligomers and polymer acrylic double bonds, which combine a high acrylate functionality and hence reactivity with possibility to incorporate tertiary amines which are known to reduce air inhibition and promote radical polymerisation. The for the dendritic acrylate oligomer or polymer according to the invention unique combination of high acrylate functionality in combination with pendant tertiary amine groups promoting polymerisation, yields an acrylate oligomer that can give excellent coating properties without the use of photoinitiators. Acrylic acid, acrylic and acrylate are above and hereinafter understood as any of the four commonly available unsaturated acids, propenoic acid (acrylic acid, vinyl formic acid), 2-methylpropenoic acid (methacrylic acid) and 2-butenic acid (crotonic acid or  $\beta$ -methyl acrylic acid) in its cis (isocrotonic acid) and trans form (crotonic acid) or as derived from derivatives and reaction products of any of said four unsaturated acids.

Dendritic acrylates have previously been disclosed in publications as above and do indeed, due to the high functionality in combination with a high molecular weight and a low viscosity, promote reactivity well above state of the art radcure oligomers and polymers. The excellent reactivity of dendritic acrylates used as starting materials according to the invention is illustrated in enclosed embodiments. However, often reactive diluents are used together with an acrylic oligomer or polymer to adjust for instance the viscosity. At high levels of reactive diluents, these might start to negatively influence the overall reactivity of a dendritic acrylate/reactive diluent formulation when cured under air atmosphere with low intensity UV lamps.

Tertiary amines are today admixed to acrylate based radiation curable formulations for two main reasons:

- i) They counteract air inhibition, provided that the particular amine contains abstractable  $\alpha$ -hydrogens, by formation of peroxy radicals, which can participate and trigger radical polymerisation of acrylic groups. Tertiary amines can therefore be used together with Norrish I type photoinitiators to reduce air inhibition and thereby increase cure speed.
- ii) They can act as co-synergists together with ketones of the benzophenone type, wherein the excited keto groups abstract a hydrogen from the amine, whereby two radicals are formed promoting radical polymerisation of acrylic groups and the like. This is the so called Norrish II type of photopolymerisation.

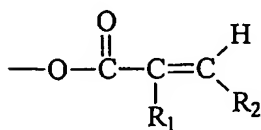
The disadvantage of admixing aliphatic or aromatic tertiary amines, for instance triethyl amine, is that large amounts of the amine, which sometimes is necessary to promote sufficient cure speed, can give blooming and migration of the amine to the surface of the cured coating. Aromatic amines can furthermore give excessive yellowing. The blooming effect can be overcome by Michael addition of a secondary amine to an conventional acrylate functional monomer or oligomer yielding so called acrylated amines. They have the advantage of promoting higher cure speed, while the blooming effect is removed due to the fact that the acrylate amine will be an integral part of the cured network. Commercial acrylated amines are available and are typically used in 5-10% by weight of a total formulation, together with 5-10 % by weight of either Norrish I or Norrish II type photoinitiators or mixtures thereof. Even though current acrylate amines are in fact prepolymers, they cannot be used as the sole oligomer or polymer component due to their adverse effects on mechanical properties compared to standard UV oligomers and polymers. Acrylated amines are further discussed in *Chemistry and Technology of UV and EB formulations for Coatings, Inks & Paints*, vol. II, Chapter IV, pp 153-157 "Acrylated Amines", by N.S. Allan, M.S. Johnsson, P.K.T. Oldring and S. Salim, SITA Technology Ltd, London, UK, 1991. In order to counteract the poor mechanical properties of low molecular weight acrylate amines, as disclosed above, attempts have been made to add secondary amines to higher molecular weight polymers. However, the

efficiency of the amine on cure speed has been reported to be significantly reduced, due to that the mobility of the amine is reduced by the high molecular weight of the formed compound - Following is quoted "Tying an amine to a prepolymer or polymer reduces the mobility of the amine group and hence its effectiveness", R. Stephen Davidson *"Exploring the Science Technology and Applications of U.V. and E.B. Curing"*, Chapter III, page 141, SITA Technology Ltd, London, UK, 1999. This was also found to be the case by R.S. Davidson, A.A. Dias and D.R. Illsey as reported in *J. Photochem Photobiol A: Chem*, 1995, 91, 153.

Amine and nitril terminated dendrimers of polyamine type are disclosed in *"Astramol™ Polypropyleneimine Dendrimers as Norrish Type II Amine Synergists"*, by J. Jansen and H. Hartwig, RadTech '98, North America, pp 207-214, wherein primary amine termination was converted to tertiary amines by Micheal addition of phenoxyethyl acrylate. The polymer backbone of the examplified dendrimers are of polyamine type. Acrylic double bonds are not present in disclosed molecules and said molecules are hence not radiation curable acrylic functional oligomers or polymers. The particular products examplified are therefore significantly different from the amine terminated dendritic acrylates according to the present invention.

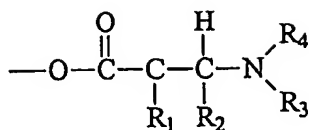
It has now been found that reported drawbacks, for instance said R. Stephen Davidson in *"Exploring the Science Technology and Applications of U.V. and E.B. Curing"*, quite surprisingly can be overcome by the use of an amine terminated dendritic acrylate according to the present invention. As will be shown in disclosed embodiments, highly reactive amine terminated dendritic acrylate coatings can be obtained, in spite of the fact that the model compounds prepared have significantly higher molecular weights than most conventional acrylate oligomers and polymers. Furthermore, the amine terminated dendritic acrylate according to the present invention yields excellent reactivity, even when diluted with excessive amounts of reactive diluents. As will be shown in the enclosed embodiments, the addition of tertiary amines to a dendritic acrylate will drastically effect the overall reactivity of a radiation curable coating even when it contains large amount of reactive diluents.

The present invention accordingly refers to a radiation curable dendritic oligomer or polymer nominally having at least one terminal group of Formula (A)



Formula (A)

and nominally at least one terminal group of Formula (B)



Formula (B)

wherein R<sub>1</sub> and R<sub>2</sub> individually are hydrogen or methyl and wherein R<sub>3</sub> and R<sub>4</sub> individually are alkyl, aryl, alkylaryl, arylalkyl, alkylalkoxy or arylalkoxy, wherein said alkyl, said alkoxy and/or said aryl optionally has one or more hydroxyl groups. Said alkyl is preferably and independently linear or branched alkanyl having 1-24 carbon atoms, linear or branched alkenyl having 3-24 carbon atoms, cycloalkanyl having 3-24 carbon atoms, branched cycloalkanyl having 4-24 carbon atoms, cycloalkenyl having 3-24 carbon atoms or branched cycloalkenyl having 4-24 carbon atoms and wherein said alkoxy preferably is ethoxy, propoxy, butoxy and/or phenylethoxy nominally comprising 0.2-50, such as 1-20 or 2-12 units of respective alkoxy. R<sub>3</sub> and R<sub>4</sub> are in especially preferred embodiment individually methyl, hydroxymethyl, ethyl, hydroxyethyl, butyl, hydroxybutyl, propyl, hydroxypropyl, pentyl, hydroxypentyl, hexyl, hydroxyhexyl, heptyl, hydroxyheptyl, octyl, hydroxyoctyl, nonyl, hydroxynonyl, phenyl or hydroxyphenyl. The nominal percentage groups of Formula (A) to groups of Formula (B) is preferably between 50:50 and 95:5, such as a nominal percentage of between 60:40 and 90:10 or 70:30 and 80:20.

The radiation curable dendritic oligomer or polymer according to the present invention can also in various embodiments, in addition to said at least one group of Formula (A) and said at least one group of formula (B), nominally comprise at least one terminal group comprising at least one oxygen, sulphur, phosphorus, nitrogen and/or halide, such as F, Cl and/or Br, atom. These embodiments include a radiation curable dendritic polymer nominally comprising at least one additional terminal hydroxyl, carboxyl, anhydride, alkenyl, ester, ether, thioester, thioether and/or thiol group.

The radiation curable dendritic oligomer or polymer of the present invention is in preferred embodiments a radiation curable dendritic polyester built up from at least one dendritic polyester, nominally having at least two terminal hydroxyl groups, which dendritic polyester *per se* is built up from ester units optionally in combination with ether units or is a radiation curable dendritic polyether built up from at least one dendritic polyether, nominally having at least two terminal hydroxyl groups, which dendritic polyether *per se* is built up from ether units optionally in combination with ester units.

Embodiments of said dendritic polyester having said at least two terminal hydroxyl groups include dendritic polyesters built up from a core molecule, having one or more hydroxyl and/or epoxide groups, and one or more dendrons bonded to said group or groups. Said

dendron preferably comprises two or more branching generations built up from at least one hydroxy and/or epoxyfunctional carboxylic acid, having at least one carboxyl group and at least two hydroxyl and/or epoxide groups, and optionally one or more spacing generations built up from at least one monohydroxy or monoepoxyfunctional monocarboxylic acid and/or from at least one lactone. Said core molecule can for instance be a 1,3-propanediol, such as a 2-alkyl-1,3-propanediol, 2,2-dialkyl-1,3-propanediol, 2-hydroxy-2-alkyl-1,3-propanediol, 2-hydroxyalkyl-2-alkyl-1,3-propanediol, 2,2-di(hydroxyalkyl)-1,3-propanediol, 2-hydroxyalkoxy-2-alkyl-1,3-propanediol, 2,2-di(hydroxyalkoxy)-1,3-propanediol or a dimer, trimer or polymer of a said 1,3-propanediol. Alkyl is here preferably and independently C<sub>1</sub>-C<sub>12</sub> alkanyl or C<sub>2</sub>-C<sub>12</sub> alkenyl and said alkoxy likewise preferably and independently ethoxy, propoxy and/or butoxy comprising 1 to 50, such as 1 to 20, units of respective alkoxy. Said core molecule can suitably be exemplified by 2-methyl-1,3-propanediol, 2-butyl-2-ethyl-1,3-propanediol, neopentyl glycol, trimethylolethane, trimethylolpropane, pentaerythritol, ditrimethylolethane, ditrimethylolpropane, dipentaerythritol and reaction products between a said 1,3-propanediol or a dimer, trimer or polymer of a said 1,3-propanediol and at least one alkylene oxide, such as a reaction product between trimethylolethane, trimethylolpropane, pentaerythritol, ditrimethylolethane, ditrimethylolpropane or dipentaerythritol and ethylene oxide, propylene oxide and/or butylene oxide, at a molar ratio alcohol to alkylene oxide of between 1:0.2 and 1:50, such as between 1:1 and 1:20. Further embodiments of said core molecule include alcohols such as ethylene glycol, propylene glycol, glycerol, anhydroennea-heptitol, 5-alkyl-5-hydroxyalkyl-1,3-dioxanes, 5,5-dihydroxyalkyl-1,3-dioxanes as well as dimers, trimers and polymers thereof and epoxides such as a glycidyl ester of a saturated monofunctional carboxylic or fatty acid having for instance 1-24 carbon atoms, a glycidyl ester of an unsaturated monofunctional carboxylic or fatty acid having for instance 3-24 carbon atoms, a glycidyl ester of a saturated or unsaturated di, tri or polyfunctional carboxylic acid having for instance 3-24 carbon atoms, a glycidyl ether of a saturated monofunctional alcohol having for instance 1-24 carbon atoms, a glycidyl ether of an unsaturated monofunctional alcohol having for instance 2-24 carbon atoms, a glycidyl ether of a saturated or unsaturated di, tri or polyfunctional alcohol having for instance 3-24 carbon atoms, a glycidyl ether of a phenol or a reaction product thereof, a glycidyl ether of a condensation product between at least one phenol and at least one aldehyde or ketone, a mono, di or triglycidyl substituted isocyanurate, an epoxide of an unsaturated monocarboxylic acid or fatty acid or corresponding triglyceride, which acid has for instance 3-24 carbon atoms, a reaction product between a glycidyl or epoxide ester or ether having x epoxide groups and a saturated or unsaturated aliphatic or cycloaliphatic carboxylic acid having y carboxylic groups, whereby x is an integer between 2-20, y is an integer between 1-10 and whereby x - y >= 1, a reaction product between a glycidyl or epoxide ester or ether having x epoxide groups and an aromatic carboxylic acid having y carboxylic groups, whereby x is an integer between 2-20, y is an integer between 1-10 and whereby x - y >= 1, a reaction

product between a glycidyl or epoxide ester or ether having x epoxide groups and an aliphatic, cycloaliphatic or aromatic hydroxyfunctional saturated or unsaturated carboxylic acid having y carboxyl groups, whereby x is an integer between 2-20, y is an integer between 1-10 and whereby  $x - y \geq 1$ , an aliphatic, cycloaliphatic or aromatic epoxypolymer, or an epoxidized polyolefine. Epoxide is here to be understood as any compound comprising at least one epoxy group.

Said dendron linked to said core comprises in especially preferred embodiments at least one generation built up from at least one di, tri or polyhydroxyfunctional monocarboxylic acid selected from the group consisting of dimethylolpropionic acid,  $\alpha,\alpha$ -bis(hydroxymethyl)butyric acid,  $\alpha,\alpha$ -bis(hydroxymethyl)valeric acid,  $\alpha,\alpha$ -bis(hydroxy)propionic acid, 3,5-dihydroxybenzoic acid,  $\alpha,\alpha,\alpha$ -tris-(hydroxymethyl)acetic acid, citric acid and/or heptonic acid and optionally at least one generation built up from at least one monohydroxyfunctional monocarboxylic acid and/or at least one lactone, such as hydroxyvaleric acid, hydroxypropionic acid, hydroxypivalic acid, glycolide,  $\delta$ -valerolactone,  $\beta$ -propiolactone and/or  $\epsilon$ -caprolactone.

Further embodiments of said dendritic polyester having said at least two terminal hydroxyl groups include polyester dendrons comprising at least one generation built up from at least one hydroxy and/or epoxyfunctional carboxylic acid, having at least one carboxyl group and at least two hydroxyl and/or epoxide groups, and optionally one or more spacing generations built up from at least one monohydroxy or monoepoxyfunctional monocarboxylic acid and/or from at least one lactone. Said polyester dendron is in its preferred embodiments equal or similar to a dendron linked to a core molecule and disclosed above.

Embodiments wherein said radiation curable dendritic oligomer or polymer is built up from a dendritic polyether having at least two terminal hydroxyl groups, include a dendritic polyether built up by thermally initiated cationic ring-opening polymerisation of at least one oxetane having at least two reactive groups of which at least one is an oxetane group. Said at least one oxetane is preferably an oxetane of a 2-alkyl-2-hydroxyalkyl-1,3-propanediol, a 2,2-di(hydroxyalkyl)-1,3-propanediol, a 2-alkyl-2-hydroxyalkoxy-1,3-propanediol, a 2,2-di(hydroxyalkoxy)-1,3-propanediol or a dimer, trimer or polymer of any of said 1,3-propanediols. Alkyl is here preferably and independently linear or branched alkanyl or alkenyl having 3 to 24, such as 4 to 12, carbon atoms and said alkoxy is preferably and independently ethoxy, propoxy or butoxy comprising 0.2 to 50, such as 1 to 20 or 2 to 12, units of respective alkoxy. Said oxetane can suitably be exemplified by oxetanes of trimethylolethane, trimethylolpropane, pentaerythritol, ditrimethylolethane, ditrimethylolpropane and dipentaerythritol and ethoxylates and/or propoxylates of a said alcohol.

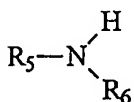


A dendritic polyester or polyether having said at least two terminal hydroxyl groups may furthermore be partially chain terminated by reaction with at least one alkanyl, cycloalkanyl, alkenyl, cycloalkenyl, alkynyl, cycloalkynyl or aryl compound selected from the group consisting of a mono, a di, a tri and a polyfunctional saturated or unsaturated carboxylic acid.

In a further aspect the present invention refers to a process for production of a radiation curable dendritic oligomer or polymer as disclosed above. Said process comprises the Steps of (i) acrylation, by addition of at least one compound having at least one acrylic double bond to a dendritic oligomer or polymer nominally having at least two terminal hydroxyl groups, said acrylation being performed at a ratio hydroxyl groups to acrylic double bonds yielding a dendritic acrylate oligomer or polymer nominally having at least one acrylic double bond, and (ii) addition of at least one secondary amine to the dendritic acrylate oligomer or polymer yielded in Step (i) at a ratio amine to acrylic double bonds yielding an amine terminated dendritic acrylate oligomer or polymer having at least one acrylic double bond and at least one tertiary amine group.

Said acrylation in Step (i) is in various embodiments of said process preferably and most suitably performed employing acrylic acid, methacrylic acid, crotonic acid, isocrotonic acid or a to a said acid corresponding anhydride or halide.

Embodiments of the present process include addition in Step (ii) of at least one secondary amine being a compound of Formula (C)



Formula (C)

wherein R<sub>5</sub> and R<sub>6</sub> individually is alkyl, aryl, alkylaryl, arylalkyl, alkylalkoxy, arylalkoxy, said alkyl and/or said aryl optionally having one or more hydroxyl groups. Alkyl is here preferably and independently linear or branched alkanyl having 1-24 carbon atoms, linear or branched alkenyl having 3-24 carbon atoms, cycloalkanyl having 3-24 carbon atoms, branched cycloalkanyl having 4-24 carbon atoms, cycloalkenyl having 3-24 carbon atoms or branched cycloalkenyl having 4-24 carbon atoms and said alkoxy is preferably ethoxy, propoxy, butoxy and/or phenylethoxy nominally comprising 0.2-50, such as 1-20 or 2-12 units of respective alkoxy. Said secondary amine is suitably exemplified by a dialkylamine or diarylamine, such as dimethylamine, methylethylamine, diethylamine, dibutylamine, diphenylamine, ethylphenylamine, cyclohexylamine, diethanolamine and diisopropanolamine.

The dendritic oligomer or polymer, nominally having said at least two terminal hydroxylgroups, of said process is in preferred embodiments a dendritic polyester built up from ester units optionally in combination with ether units or a dendritic polyether built up from ether units optionally in combination with ester units as herein previously disclosed, discussed and exemplified.

In yet a further aspect, the present invention refers to a radiation curable composition comprising a radiation curable dendritic oligomer or polymer as previously disclosed in an amount of at least 0.1%, such as 0.5-80%, 0.5-50% or 1-25%, by weight. Said composition comprises optionally in addition to said radiation curable dendritic oligomer or polymer comprises at least one linear or branched radiation curable monomer, oligomer or polymer, such as at least one linear or branched acrylic monomer, oligomer or polymer having at least one, preferably at least two acrylic double bonds and/or

Embodiments of said composition of the present invention include compositions comprising, in addition to said radiation curable dendritic oligomer or polymer, at least one reactive diluent, such as at least one acrylic ester of a 2-alkyl-1,3-propanediol, a 2,2-dialkyl-1,3-propanediol, a 2-hydroxy-2-alkyl-1,3-propanediol, a 2-hydroxyalkyl-2-alkyl-1,3-propanediol, a 2,2-di(hydroxyalkyl)-1,3-propanediol, a 2-hydroxyalkoxy-2-alkyl-1,3-propanediol or a 2,2-di(hydroxyalkoxy)-1,3-propanediol. Alkyl is here independently C<sub>1</sub>-C<sub>12</sub> alkanyl or C<sub>2</sub>-C<sub>12</sub> alkenyl and alkoxy likewise independently ethoxy, propoxy or butoxy nominally comprising 0.2 to 50, such as 1 to 20 or 2 to 12, units of respective alkoxy. Said reactive diluent is in especially preferred embodiments an acrylic ester of 2-methyl-1,3-propanediol, 2-ethyl-2-butyl-1,3-propanediol, neopentyl glycol, trimethylolethane, trimethylolpropane, pentaerythritol, ditrimethylolethane, ditrimethylolpropane or dipentaerythritol or an acrylic ester of a reaction product between at least one alkylene oxide, such as ethylene oxide, propylene oxide and/or butylene oxide, and 2-methyl-1,3-propanediol, 2-ethyl-2-butyl-1,3-propanediol, neopentyl glycol, trimethylolethane, trimethylolpropane, pentaerythritol, ditrimethylolethane, ditrimethylolpropane or dipentaerythritol at a molar ratio alcohol to alkylene oxide of between 1:0.2 and 1:50, such as between 1:1 and 1:20.

The composition of the present invention can, furthermore, comprise at least one Norrish I or Norrish II type photoinitiator, preferably in an amount of at most 1% by weight and/or at least one acrylated amine, preferably in an amount of at most 10%, such as 5-10%, by weight of the total formulation. Said acrylated amine is preferably of the type disclosed and discussed in *Chemistry and Technology of UV and EB formulations for Coatings, Inks & Paints*, vol. II, Chapter IV, pp 153-157 "Acrylated Amines", by N.S. Allan, M.S. Johnsson, P.K.T. Oldring and S. Salim, SITA Technology Ltd, London, UK, 1991.

Without further elaboration, it is believed that one skilled in the art can, using the preceding description, utilise the present invention to its fullest extent. The following preferred specific embodiment Examples 1-6 are, therefore, to be construed as merely illustrative and not limitative of the remainder of the disclosure in any way whatsoever. In the following Examples 1-6 and Graphs 1-9 illustrate and give:

Example 1: Preparation of a dendritic polyester acrylate according to an embodiment of Step (i) of the process of the present invention.

Example 2 and 3: Preparation of an embodiment of a dendritic oligomer/polymer according to the present invention. Preparation is performed according to an embodiment of the process of the present invention.

Examples 4-6: Evaluations of products obtained according to Examples 1-3 in comparison with reference substances.

Graph 1: Chemical resistance of dendritic acrylates vs. conventional oligomer acrylates as a function of number of passages under irradiation source.

Graph 2: Pencil hardness of cured dendritic acrylate oligomers vs. reference acrylates with and without acrylate amine.

Graph 3: Film hardness (pendulum hardness) of dendritic acrylate oligomers vs. reference acrylates with and without acrylate amine. Pendulum hardness is measured using a König pendulum and reported as König seconds.

Graph 4: Chemical resistance of diluted dendritic acrylates and reference acrylates.

Graph 5: Scratch resistance of diluted dendritic acrylates and reference acrylates.

Graph 6: Film hardness of PEOTA-diluted dendritic acrylates and reference acrylates.

Graph 7: Chemical resistance of diluted dendritic acrylate and reference acrylate when admixing 0.1% of benzophenone to a coating formulation.

Graph 8: Scratch resistance of diluted dendritic acrylates and reference acrylate with addition of 0.1% benzophenone.

Graph 9: Film hardness of diluted dendritic acrylates and reference acrylate/amine with 0.1% addition of benzophenone.

While particular embodiments of the invention is shown, it will be understood, of course, that the invention is not limited thereto since many modifications may be made, and it is, therefore, contemplated to cover by the appended claims any such modifications as fall within the true scope of the invention.

**Example 1**

200.0 g of a commercially available hydroxyl functional dendritic polymer of polyester type (Boltorn® H20, Perstorp Specialty Chemicals, Sweden), having a nominal hydroxyl value of 510 mg KOH/g and a nominal molecular weight of 1750 g/mole, and 350 ml of toluene were charged in a 2 l reaction flask equipped with a Teflon™ lined glass stirrer, an oilbath, air inlet, a cooler and a Dean-Stark device for removal of reaction water. The mixture was heated to 100°C. 144.5 g of acrylic acid, 0.48 g of nitrobenzene and 3.44 g of 4-methoxyphenol were subsequently charged and air was allowed to pass through the reaction mixture which was further heated to 110°C whereby 3.44 g of methane sulphonic acid was added to catalyse the esterification reaction. The temperature of the reaction mixture was now during 25 minutes allowed to increase from 110 to 120°C. Reaction water begun to evaporate at said temperature and the reaction temperature was gradually increased during 9 hours to 135°C at which temperature the reaction mixture had reached an acid value of 26.5 mg KOH/g. The reaction was now terminated by a temperature reduction to 70°C and 300 g of  $Al_2O_3$  (s) and 200 ml of toluene were added. The mixture was passed through a pressure filter to remove the aluminium compounds including formed aluminium oxide acrylate salt. The final product was recovered by removal of solvent in a rotary evaporator under air atmosphere.

The obtained dendritic acrylate exhibited following product characteristics:

|                                     |        |
|-------------------------------------|--------|
| Molecular weight (nominal), g/mole: | 2 614  |
| Acrylate functionality, eq:         | 16     |
| Acrylate concentration, mmole/g:    | 6.12   |
| Final acid value, mg KOH/g:         | 1.6    |
| Viscosity, Brookfield, 23°C, mPas:  | 54 000 |
| Non-volatile content, %:            | 95     |

**Example 2**

75.0 g of the dendritic acrylate obtained in Example 1 was charged in a reaction flask equipped with a stirrer, a heater, temperature control, nitrogen inlet and a cooler. 8.90 g of dibutylamine (15 mole% on acrylic unsaturation) was charged and the reaction mixture was heated to 50°C. Said temperature was maintained for 120 minutes. The reaction mixture was now cooled to room temperature. Obtained amine terminated dendritic acrylate was a viscous yellow, transparent liquid with a faint acidic odour (no amine odour) and exhibited the following product characteristics:

|  |       |
|--|-------|
| Molecular weight (nominal), g/mole:          | 2 924 |
| Amine content (as bonded amine) % by weight: | 10.6  |
| Acrylate functionality, eq:                  | 13.6  |
| Acrylate concentration, mmole/g:             | 4.65  |

### Example 3

Example 2 was repeated with the difference that 20 mole% of dibutylamine instead of 15 mole% was charged. Obtained amine terminated dendritic acrylate was a highly viscous, yellow and odour-free product at room temperature and exhibited following product characteristics:

|  |       |
|--|-------|
| Molecular weight (nominal), g/mole:          | 3 028 |
| Amine content (as bonded amine) % by weight: | 13.7  |
| Acrylate functionality, eq:                  | 12.8  |
| Acrylate concentration, mmole/g:             | 4.22  |

### Example 4

The products obtained in Examples 1-3 were heated to 50°C and then coated with a Meyer "2" bar to a film thickness of 12 µm on steel panels of the dimensions 152 x 75 x 0.25 mm.

Two references were also evaluated. One of said references was a commercial polyester oligomer/polymer acrylate (1000 g/mole, 4 mmole/g of unsaturation) of high reactivity. The second was a mixture of 90 pph of the commercial reference according to above and 10 pph of a commercial acrylate amine, of the type disclosed in *Chemistry and Technology of UV and EB formulations for Coatings, Inks & Paints*, vol. II, Chapter IV, 157 "Acrylated Amines", by N.S. Allan, M.S. Johnsson, P.K.T. Oldring and S. Salim, SITA Technology Ltd, London, UK, 1991, to represent a system with equal amount of amine in weight per cent in comparison with the dendritic product according to Example 2. The coated panels were passed 2, 4 and 8 times, respectively for each coating, at a belt speed of 20 m/min under an 80W/cm medium pressure mercury lamp in air atmosphere.

Obtained film properties of evaluated oligomers/polymers are given in Graphs 1 to 4 below. It is evident from said graphs that all dendritic acrylate oligomers/polymers show remarkable reactivity without the use of photoinitiators and yield coatings with exceptional chemical resistance, scratch resistance (pencil hardness) and film hardness. It is also obvious from in

said graphs given result that the incorporation of tertiary amine to the dendritic structure does not impart the obtained coating properties compared to the neat dendritic acrylate. The conventional oligomer/polymer acrylate does also cure to some extent but yield very poor chemical resistance. The presence of a conventional acrylate amine in an amount of 10 pph does not contribute to any improvement in the film properties obtained.

#### **Example 5**

Coating formulations comprising the products obtained in Examples 1-3 were prepared. Respective dendritic oligomer/polymer were diluted with pentaerythritol ethoxylate tetraacrylate (PEOTA) as reactive diluent in a 1:1 weight ratio. The reactive diluent content was hence 50% by weight of the total formulations. The reference oligomer/polymer described and evaluated in Example 4 were also in the same manner diluted with PEOTA to a reactive diluent content of 50% by weight.

Prepared coating formulations were coated in the same manner as described in Example 4 and also evaluated in exactly the same way using the same UV equipment. Obtained film properties of the cured coatings are given in Graphs 4-6 below.

Improvements obtained when using a radiation curable dendritic polymer (an amine terminated dendritic acrylate) in accordance with the present invention in diluted coating formulations are apparent from the results given in said Graphs 4-6. The PEOTA diluted amine terminated dendritic acrylate according to Example 2 exhibited excellent chemical resistance (8 passages under the UV-lamp) without the use of photoinitiator. The other coatings did not show any significant chemical resistance when diluted in the reactive diluent. Very scratch resistant films are, furthermore, obtained when the diluted product according to Example 2 is passed 8 times under the UV-lamp. A pencil hardness of 6H-7H is harder than what the majority of known radiation curable coatings can give using excessive amounts of photoinitiator. Cured films of good film hardness were also obtained without the use of photoinitiator with said diluted product according to Example 2.

#### **Example 6**

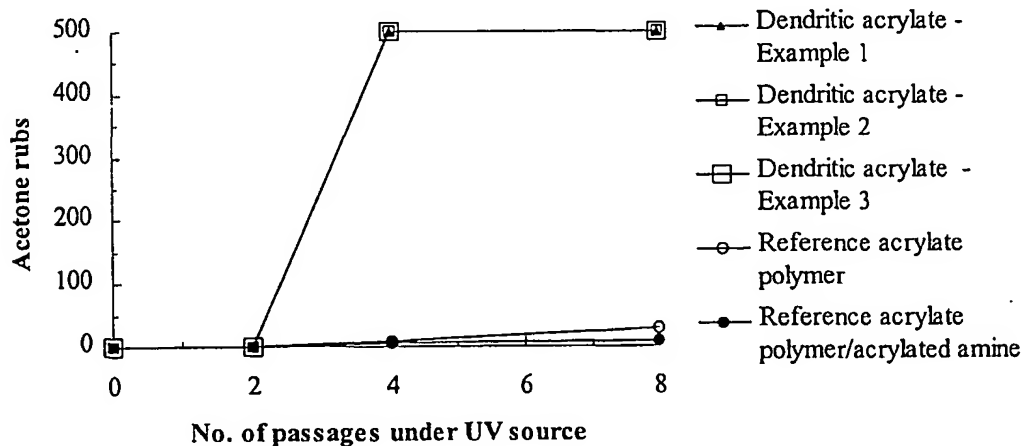
This example is an extension of Example 5 and exemplifies that extremely reactive coatings can be obtained according to the invention, when large amounts of reactive diluents are present, by minute additions of a photoinitiator. The diluted dendritic acrylate according to Example 2 were evaluated in the presence of a very low amount of photoinitiator. 0.1% by weight of benzophenone was added to said diluted dendritic acrylate and compared with the diluted reference (see Example 4) comprising acrylate amine. Coatings were prepared and

evaluated in the same manner as described in Example 4. Obtained film properties are given in Graphs 7-9 below.

Graphs 7-9 again confirm the unique performance of radiation curable coatings comprising amine terminated dendritic acrylates according to the present invention. A very small addition (0.1% by weight - normally used levels of benzophenone in radiation curing coatings are approx. 5% by weight) of benzophenone yields coatings having extremely good chemical resistance, very good scratch resistance as well as high film hardness. The coatings comprising an amine terminated dendritic acrylate according to the present invention yield - with or without photoinitiator - coating properties that are superior to coatings based on state of the art commercial technology.

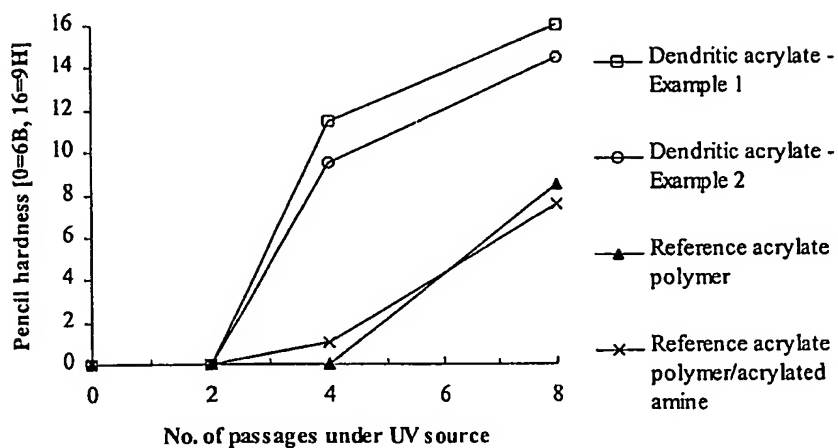
Graph 1

UV-curing of neat oligomers in air at 20m/min, 80W/cm, No PI



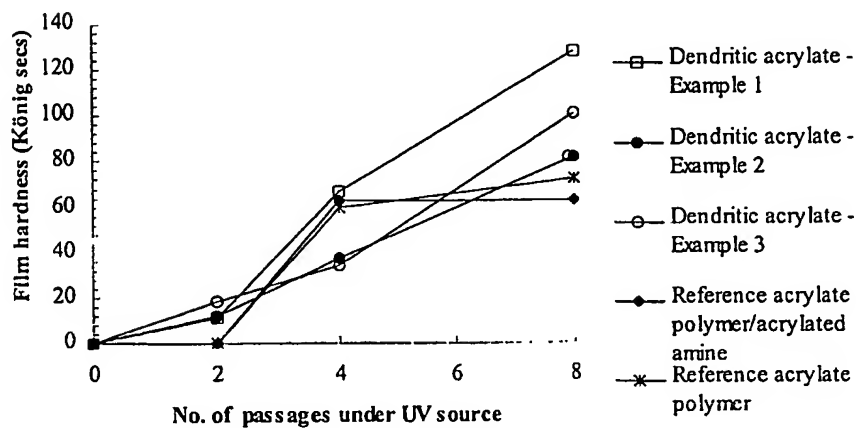
Graph 2

UV-curing of neat oligomers in air at 20m/min, 80W/cm,  
No PI



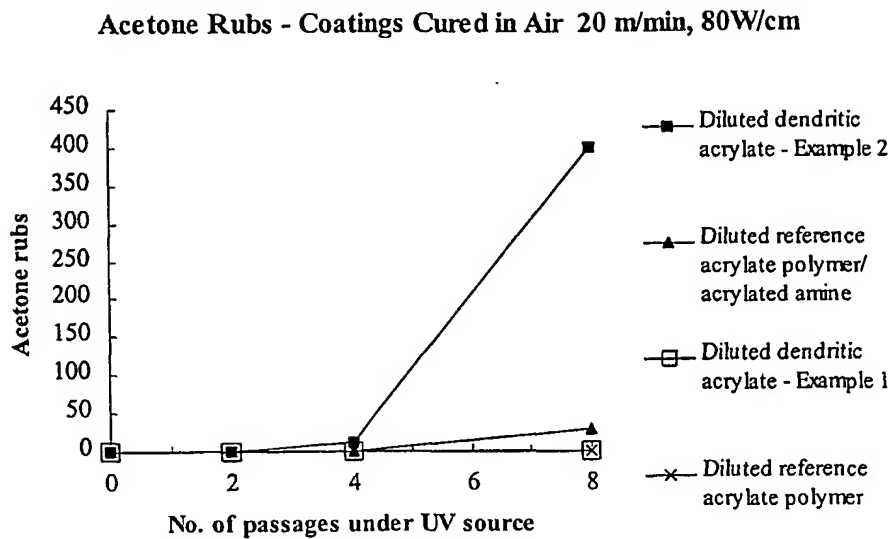
Graph 3

UV Curing No Photoinitiator - Air, 20 m/min, 80W/cm

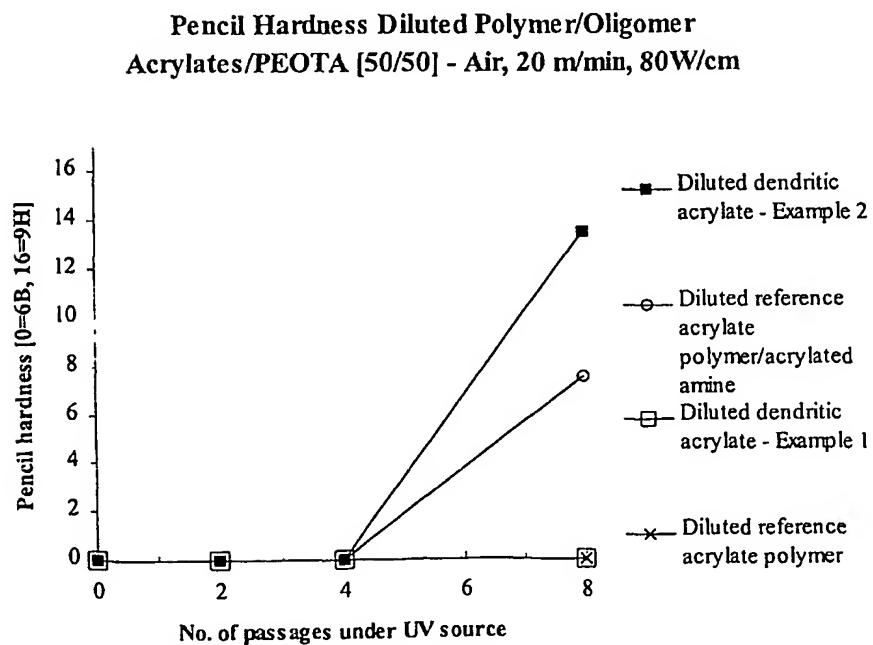




Graph 4

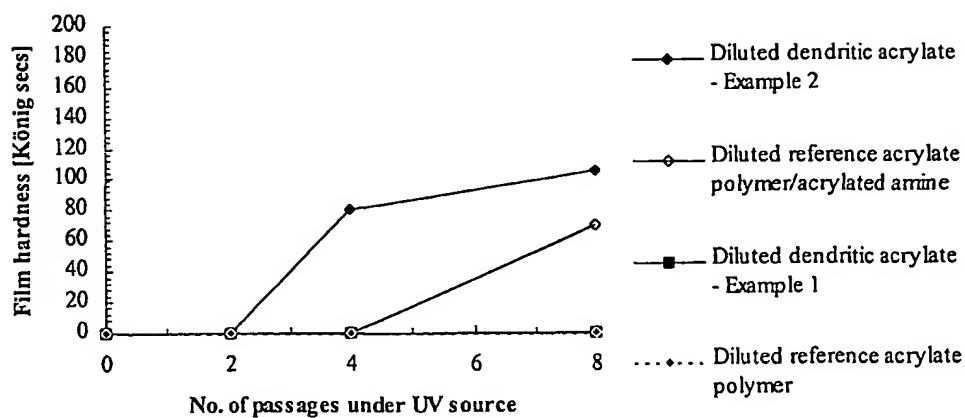


Graph 5



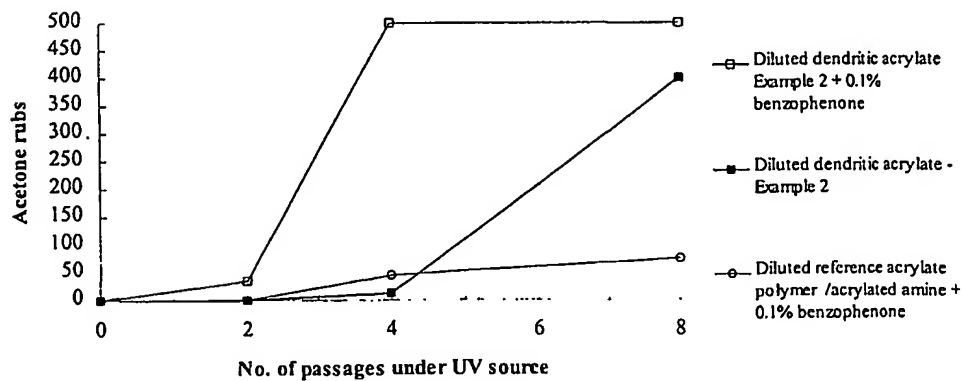
Graph 6

UV Curing of Diluted Polymer/Oligomer Acrylates/  
PEOTA [50/50] - Air, 20 m/min, 80W/cm

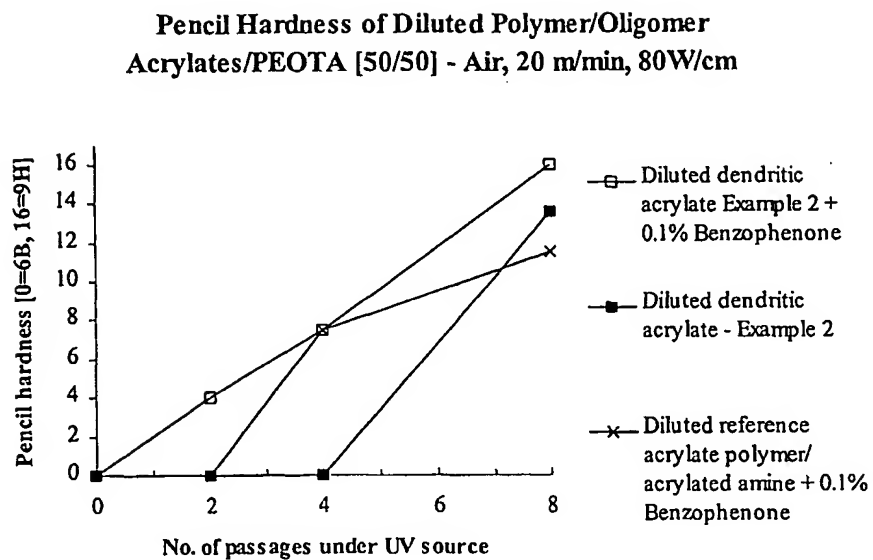


Graph 7

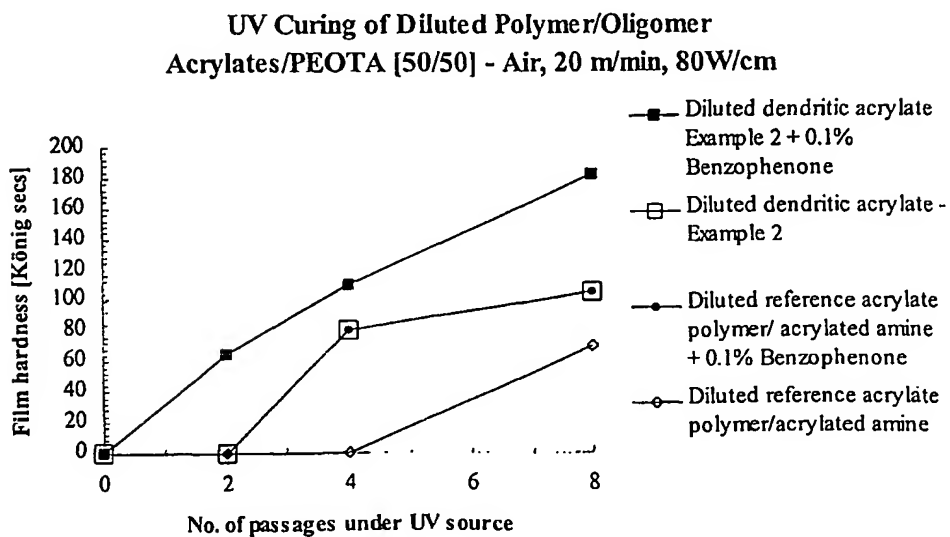
Acetone rubs of coatings cured in air at 20 m/min, 80W/cm



Graph 8

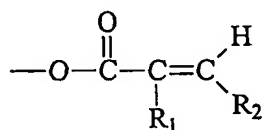


Graph 9



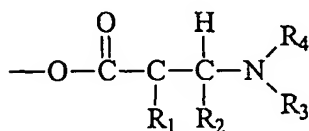
## CLAIMS

1. A radiation curable dendritic oligomer or polymer  
**characterised in**, that said radiation curable dendritic oligomer or polymer  
 nominally has at least one terminal group of Formula (A)



Formula (A)

and nominally at least one terminal group of Formula (B)



Formula (B)

wherein R<sub>1</sub> and R<sub>2</sub> individually are hydrogen or methyl and wherein R<sub>3</sub> and R<sub>4</sub> individually are alkyl, aryl, alkylaryl, arylalkyl, alkylalkoxy, arylalkoxy, said alkyl and/or said aryl optionally having one or more hydroxyl groups.

2. A radiation curable dendritic oligomer or polymer according to Claim 1  
**characterised in**, that said alkyl indenpendently is linear or branched alkanyl  
 having 1-24 carbon atoms, linear or branched alkenyl having 3-24 carbonatoms,  
 cycloalkanyl having 3-24 carbon atoms, branched cycloalkanyl having 4-24 carbon  
 atoms, cycloalkenyl having 3-24 carbon atoms or branched cycloalkenyl having 4-24  
 carbon atoms and said alkoxy is ethoxy, propoxy, butoxy and/or phenylethoxy nominally  
 comprising 0.2-50, such as 1-20 or 2-12 units of respective alkoxy.
3. A radiation curable dendritic oligomer or polymer according to Claim 1 or 2  
**characterised in**, that R<sub>3</sub> and R<sub>4</sub> individually is methyl, hydroxymethyl, ethyl,  
 hydroxyethyl, butyl, hydroxybutyl, propyl, hydroxypropyl, pentyl, hydroxypentyl, hexyl,  
 hydroxyhexyl, heptyl, hydroxyheptyl, octyl, hydroxyactyl, nonyl, hydroxynonyl, phenyl  
 or hydroxyphenyl.
4. A radiation curable dendritic oligomer or polymer according to any of the Claims 1-3  
**characterised in**, a nominal percentage groups of Formula (A) to groups of  
 Formula (B) of between 50:50 and 95:5, such as a nominal percentage of between 60:40  
 and 90:10 or 70:30 and 80:20.

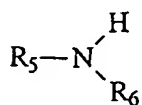
5. A radiation curable dendritic oligomer or polymer according to any of the Claims 1-4 **characterised in**, that said radiation curable dendritic oligomer or polymer in addition to said at least one group of Formula (A) and said at least one group of formula (B) nominally comprises at least one terminal group comprising at least one oxygen, sulphur, phosphorous, nitrogen and/or halide, such as F, Cl and/or Br, atom.
6. A radiation curable dendritic oligomer or polymer according to any of the Claims 1-5 **characterised in**, that said radiation curable dendritic oligomer or polymer in addition to said at least one group of Formula (A) and said at least one group of formula (B) nominally comprises at least one terminal hydroxyl, carboxyl, anhydride, alkenyl, ester, ether, thioester, thioether, and/or thiol group.
7. A radiation curable dendritic oligomer or polymer according to any of the Claims 1-6 **characterised in**, that said radiation curable dendritic oligomer or polymer is built up from at least one dendritic polyester, nominally having at least two terminal hydroxyl groups, being built up from ester units optionally in combination with ether units.
8. A radiation curable dendritic oligomer or polymer according to Claim 7 **characterised in**, that said dendritic polyester having said at least two hydroxyl groups is built up from a core molecule, having one or more hydroxyl or epoxide groups, and one or more dendrons bonded to said group or groups, said dendron comprising two or more branching generations built up from at least one hydroxy and/or epoxyfunctional carboxylic acid, having at least one carboxyl group and at least two hydroxyl and/or epoxide groups, and optionally one or more spacing generations built up from at least one monohydroxy or monoepoxyfunctional monocarboxylic acid and/or from at least one lactone.
9. A radiation curable dendritic oligomer or polymer according to Claim 8 **characterised in**, that said core molecule is a 1,3-propanediol, such as a 2-alkyl-1,3-propanediol, a 2,2-dialkyl-1,3-propanediol, a 2-hydroxy-2-alkyl-1,3-propanediol, a 2-hydroxyalkyl-2-alkyl-1,3-propanediol, a 2,2-di(hydroxyalkyl)-1,3-propanediol, a 2-hydroxyalkoxy-2-alkyl-1,3-propanediol or a 2,2-di(hydroxyalkoxy)-1,3-propanediol.
10. A radiation curable dendritic oligomer or polymer according to Claim 8 **characterised in**, that said said core molecule is a dimer, trimer or polymer of a 2-alkyl-1,3-propanediol, a 2,2-dialkyl-1,3-propanediol, a 2-hydroxy-2-alkyl-1,3-propanediol, a 2-hydroxyalkyl-2-alkyl-1,3-propanediol, a 2,2-di(hydroxyalkyl)-1,3-propanediol, a 2-hydroxyalkoxy-2-alkyl-1,3-propanediol or a 2,2-di(hydroxyalkoxy)-1,3-propanediol.

11. A radiation curable dendritic oligomer or polymer according to Claim 9 or 10  
**characterised in**, that said alkyl independently is C<sub>1</sub>-C<sub>12</sub> alkanyl or C<sub>2</sub>-C<sub>12</sub> alkenyl and that said alkoxy independently is ethoxy, propoxy or butoxy nominally comprising 0.2 to 50, such as 1 to 20 or 2 to 12, units of respective alkoxy.
12. A radiation curable dendritic oligomer or polymer according to any of the Claims 8-11  
**characterised in**, that said core molecule is 2-methyl-1,3-propanediol, 2-butyl-2-ethyl-1,3-propanediol, neopentyl glycol, trimethylolethane, trimethylolpropane, pentaerythritol, ditrimethylolethane, ditrimethylolpropane or dipentaerythritol.
13. A radiation curable dendritic oligomer or polymer according to any of the Claims 8-11  
**characterised in**, that said core molecule is a reaction product between trimethylolethane, trimethylolpropane, pentaerythritol, ditrimethylolethane, ditrimethylolpropane or dipentaerythritol and at least one alkylene oxide, such as ethylene oxide, propylene oxide or butylene oxide, at a molar ratio alcohol to alkylene oxide of between 1:0.2 and 1:50, such as between 1:1 and 1:20.
14. A radiation curable dendritic oligomer or polymer according to any of the Claims 8-11  
**characterised in**, that said core molecule is an epoxide, such as a glycidyl ester of a saturated or unsaturated mono, di, tri or polyfunctional carboxylic or fatty acid, a glycidyl ether of a saturated or unsaturated mono, di, tri or polyfunctional alcohol, a glycidyl ether of a phenol or a reaction product thereof, a glycidyl ether of a condensation product between at least one phenol and at least one aldehyde or ketone, a mono, di or triglycidyl substituted isocyanurate, an epoxide of an unsaturated monocarboxylic acid or fatty acid or corresponding triglyceride or an epoxidized polyolefine.
15. A radiation curable dendritic oligomer or polymer according to any of the Claims 8-14  
**characterised in**, that said dendron comprises at least one generation built up from at least one di, tri or polyhydroxyfunctional monocarboxylic acid selected from the group consisting of dimethylolpropionic acid,  $\alpha,\alpha$ -bis(hydroxymethyl)butyric acid,  $\alpha,\alpha$ -bis(hydroxymethyl)valeric acid,  $\alpha,\alpha$ -bis(hydroxy)propionic acid, 3,5-dihydroxybenzoic acid,  $\alpha,\alpha,\alpha$ -tris(hydroxymethyl)acetic acid, citric acid and/or heptonic acid.
16. A radiation curable dendritic oligomer or polymer according to any of the Claims 8-15  
**characterised in**, that said dendron comprises at least one generation built up from at least one monohydroxyfunctional monocarboxylic acid and/or at least one lactone, such as hydroxyvaleric acid, hydroxypropionic acid, hydroxypivalic acid, glycolide,  $\delta$ -valerolactone,  $\beta$ -propiolactone and/or  $\epsilon$ -caprolactone.

17. A radiation curable dendritic oligomer or polymer according to Claim 7  
**characterised in**, that said radiation curable dendritic oligomer or polymer is built up from at least one polyester dendron, nominally having at least to terminal hydroxyl groups, comprising at least one generation being built up from at least one hydroxy and/or epoxyfunctional carboxylic acid, having at least one carboxyl group and at least two hydroxyl and/or epoxide groups, and optionally one or more spacing generations built up from at least one monohydroxy or monoepoxyfunctional monocarboxylic acid and/or from at least one lactone.
18. A radiation curable dendritic oligomer or polymer according to Claim 17  
**characterised in**, that said polyester dendron comprises at least one generation built up from at least one di, tri or polyhydroxyfunctional monocarboxylic acid, such as dimethylolpropionic acid,  $\alpha,\alpha$ -bis(hydroxymethyl)butyric acid,  $\alpha,\alpha$ -bis(hydroxymethyl)-valeric acid,  $\alpha,\alpha$ -bis(hydroxy)propionic acid, 3,5-dihydroxybenzoic acid,  $\alpha,\alpha,\alpha$ -tris(hydroxymethyl)-acetic acid, citric acid and/or heptonic acid.
19. A radiation curable dendritic oligomer or polymer according to Claim 17 or 18  
**characterised in**, that said polyester dendron comprises at least one generation built up from at least one monohydroxyfunctional monocarboxylic acid and/or at least one lactone, such as hydroxyvaleric acid, hydroxypropionic acid, hydroxypivalic acid, glycolide,  $\delta$ -valerolactone,  $\beta$ -propiolactone and/or  $\epsilon$ -caprolactone.
20. A radiation curable dendritic oligomer or polymer according to any of the Claims 1-6  
**characterised in**, that said radiation curable dendritic oligomer or polymer is built up from a dendritic polyether, nominally having at least two terminal hydroxyl groups, being built up from ether units optionally in combination with ester units.
21. A radiation curable dendritic oligomer or polymer according to Claim 20  
**characterised in**, that said dendritic polyether having said at least two hydroxyl groups is built up by thermally initiated cationic ring-opening polymerisation of at least one oxetane having at least two reactive groups of which at least one is an oxetane group.
22. A radiation curable dendritic oligomer or polymer according to Claim 21  
**characterised in**, that said at least one oxetane is an oxetane of a 2-alkyl-2-hydroxyalkyl-1,3-propanediol, a 2,2-di(hydroxyalkyl)-1,3-propanediol, a 2-alkyl-2-hydroxyalkoxy-1,3-propanediol, a 2,2-di(hydroxyalkoxy)-1,3-propanediol or a dimer, trimer or polymer of a said 1,3-propanediol.
23. A radiation curable dendritic oligomer or polymer according to Claim 22  
**characterised in**, that said alkyl independently is linear or branched alkanyl or

alkenyl having 3 to 24, such as 4 to 12, carbon atoms and that said alkoxy independently is ethoxy, propoxy or butoxy comprising 0.2 to 50, such as 1 to 20 or 2 to 12, units of respective alkoxy.

24. A radiation curable dendritic oligomer or polymer according to Claim 22 or 23  
c h a r a c t e r i s e d i n, that said at least one oxetane is an oxetane of trimethylolethane, trimethylolpropane, pentaerythritol, ditrimethylolethane, ditrimethylolpropane or dipentaerythritol.
25. A radiation curable dendritic oligomer or polymer according to any of the Claims 7-24  
c h a r a c t e r i s e d i n, that said dendritic polyester or polyether is partially chain terminated by reaction with at least one alkanyl, cycloalkanyl, alkenyl, cycloalkenyl, alkynyl, cycloalkynyl or aryl compound selected from the group consisting of a mono, a di, a tri and a polyfunctional saturated or unsaturated carboxylic acid.
26. A process for production of a radiation curable dendritic oligomer or polymer according to any of the Claims 1-25  
c h a r a c t e r i s e d i n, that said process comprises the Steps of
  - i) Acrylation of a dendritic oligomer or polymer nominally having at least two terminal hydroxyl groups, said acrylation being performed by addition of at least one compound having at least one acrylic double bond to at least one said hydroxyl group and said acrylation being performed at a ratio hydroxyl groups to acrylic double bonds yielding a dendritic acrylate oligomer or polymer nominally having at least one acrylic double bond, and
  - ii) addition of at least one secondary amine to the dendritic acrylate polymer yielded in Step (i), said addition being performed at a ratio amine to acrylic double bonds yielding an amine terminated dendritic acrylate oligomer or polymer having at least one acrylic double bond and at least one tertiary amine group.
27. A process according to Claim 26  
c h a r a c t e r i s e d i n, that said acrylation in Step (i) is performed employing acrylic acid, methacrylic acid, crotonic acid, isocrotonic acid or a to a said acid corresponding anhydride or halide.
28. A process according to Claim 26 or 27  
c h a r a c t e r i s e d i n, that said at least one secondary amine added in Step (ii) is a compound of Formula (C)



Formula (C)



wherein  $R_5$  and  $R_6$  individually is alkyl, aryl, alkylaryl, arylalkyl, alkylalkoxy, arylalkoxy, said alkyl and/or said aryl optionally having one or more hydroxyl groups.

29. A process according to Claim 28  
characterised in, that said alkyl independently is linear or branched alkanyl having 1-24 carbon atoms, linear or branched alkenyl having 3-24 carbon atoms, cycloalkanyl having 3-24 carbon atoms, branched cycloalkanyl having 4-24 carbon atoms, cycloalkenyl having 3-24 carbon atoms or branched cycloalkenyl having 4-24 carbon atoms and that said alkoxy preferably is ethoxy, propoxy, butoxy and/or phenylethoxy nominally comprising 0.2-50, such as 1-20 or 2-12 units of respective alkoxy.
30. A process according to any of the Claims 26-29  
characterised in, that said secondary amine is a dialkylamine or diarylamine selected from the group consisting of dimethylamine, methylethylamine, diethylamine, dibutylamine, diphenylamine, ethylphenylamine, cyclohexylamine, diethanolamine, diisopropanolamine.
31. A radiation curable composition comprising a radiation curable dendritic oligomer or polymer according to any of the Claims 1-25  
characterised in, that said radiation curable dendritic polymer is present in said composition in an amount of at least 0.1% by weight.
32. A radiation curable composition according to Claim 31  
characterised in, that said radiation curable dendritic oligomer or polymer is present in said composition in an amount of 0.5-80%, such as 0.5-50% or 1-25% by weight.
33. A radiation curable composition according to Claim 31 or 32  
characterised in, that said composition in addition to said radiation curable dendritic oligomer or polymer comprises at least one linear or branched radiation curable monomer, oligomer or polymer.
34. A radiation curable composition according to Claim 33  
characterised in, that said at least one linear or branched monomer, oligomer or polymer is at least one linear or branched acrylic monomer, oligomer or polymer having at least one, preferably at least two acrylic double bonds.
35. A radiation curable composition according to Claim 31 or 32  
characterised in, that said composition in addition to said radiation curable dendritic oligomer or polymer comprises at least one reactive diluent.

36. A radiation curable composition according to Claim 35  
c h a r a c t e r i s e d i n, that said reactive diluent is an acrylic ester of a 2-alkyl-1,3-propanediol, a 2,2-dialkyl-1,3-propanediol, a 2-hydroxy-2-alkyl-1,3-propanediol, a 2-hydroxyalkyl-2-alkyl-1,3-propanediol, a 2,2-di(hydroxyalkyl)-1,3-propanediol, a 2-hydroxyalkoxy-2-alkyl-1,3-propanediol or a 2,2-di(hydroxyalkoxy)-1,3-propanediol.
37. A radiation curable composition according to Claim 36  
c h a r a c t e r i s e d i n, that said alkyl independently is C<sub>1</sub>-C<sub>12</sub> alkanyl or C<sub>2</sub>-C<sub>12</sub> alkenyl and that said alkoxy independently is ethoxy, propoxy or butoxy nominally comprising 0.2 to 50, such as 1 to 20 or 2 to 12, units of respective alkoxy.
38. A radiation curable composition according to any of the Claims 35-37  
c h a r a c t e r i s e d i n, that said reactive diluent is an acrylic ester of 2-methyl-1,3-propanediol, 2-ethyl-2-butyl-1,3-propanediol, neopentyl glycol, trimethylolethane, trimethylolpropane, pentaerythritol, ditrimethylolethane, ditrimethylolpropane or dipentaerythritol.
39. A radiation curable composition according to any of the Claims 35-37  
c h a r a c t e r i s e d i n, that said reactive diluent is an acrylic ester of a reaction product between at least one alkylene oxide and 2-methyl-1,3-propanediol, 2-ethyl-2-butyl-1,3-propanediol, neopentyl glycol, trimethylolethane, trimethylolpropane, pentaerythritol, ditrimethylolethane, ditrimethylolpropane or dipentaerythritol at a molar ratio alcohol to alkylene oxide of between 1:0.2 and 1:50, such as between 1:1 and 1:20.
40. A radiation curable composition according to Claim 39  
c h a r a c t e r i s e d i n, that said alkylene oxide is ethylene oxide, propylene oxide and/or butylene oxide.
41. A radiation curable composition according to any of the Claims 33- 40  
c h a r a c t e r i s e d i n, that said radiation curable composition comprises at least one Norrish I or Norrish II type photoinitiator.
42. A radiation curable composition according to Claim 41  
c h a r a c t e r i s e d i n, that said photoinitiator is present in an amount of at most 1% by weight.
43. A radiation curable composition according to any of the Claims 33- 40  
c h a r a c t e r i s e d i n, that said radiation curable composition comprises at least one acrylated amine, preferably in an amount of at most 10%, such as 5-10%, by weight.

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